TABLE 4-continued

Concentration in Parts per Thousand of:		Days Stored before Any
HF	H_2ZrF_6	Visible Precipitate Formed
0.75	5.0	>30
1.0	3.0	>30
1.0	5.0	>30
1.0	75	>30
1.0	10	>30

The results in Table 4 indicate that at least 0.50 ppt of HF is required to stabilize a composition that contains at least 5.0 ppt of H_2ZrF_6 against formation of a precipitate during storage under practical use conditions.

The invention claimed is:

1. A composition for coating or touching up or both coating and touching up a metal surface, said composition comprising water and:

(A) from about 0.5 millimoles per kilogram to about 240 millimoles per kilogram, a unit hereafter abbreviated as "mM/kg" of a component of fluorometallate anions, each of said anions consisting of:

(i) at least four fluorine atoms; and

(ii) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron, and, optionally, one or both of

(iii) at least one ionizable hydrogen atom; and

(iv) at least one oxygen atom;

(B) from about 0.5 grams/liter to about 10 grams/liter, a unit hereafter abbreviated as g/l, of a component of phosphorus-containing inorganic oxyanions or phosphonate anions or both phosphorus-containing inorganic oxyanions and phosphonate anions calculated as the stoichiometric equivalent of H_3PO_4; and

(C) from about 0.5 g/l to about 3.5 g/l of hexavalent chromium,

(D) from about 0.10 g/l to about 2.20 g/l of trivalent chromium cations;

said liquid composition comprising not more than 0.06% of dispersed silica and silicates.

2. The composition according to claim 1, wherein:

the fluorometallate anions are selected from the group consisting of fluorosilicate, fluorotitanate, and fluorozirconate anions.

3. The composition according to claim 1, wherein:

the fluorometallate anions include fluorozirconate anions;

the concentration of fluorozirconate anions is within a range from about 3.5 to about 6.0 mM/kg, inclusive of 3.5 and 6.0 mM/kg;

the total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4 is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the concentration of hexavalent chromium is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

the concentration of chromium(III) cations is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l;

wherein a ratio of hexavalent chromium to chromium(III) ions is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00.

4. The composition according to claim 3 which further includes fluorinated alkyl ester surfactant molecules in a concentration that is within a range from about 0.070 to about 0.13 parts per thousand, at unit hereinafter abbreviated as "ppt", said range being inclusive of 0.070 and 0.13 ppt.

5. The composition according to claim 1, wherein:

the fluorometallate anions include fluorozirconate anions;

the concentration of fluorozirconate anions is within a range from about 18.0 to about 30.0 mM/kg, inclusive of 18.0 and 30.0 mM/kg;

the total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4 is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the concentration of hexavalent chromium is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

the concentration of chromium(III) cations is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l;

wherein a ratio of hexavalent chromium to chromium(III) ions is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00; and further including from about 0.70 ppt to about 1.3 ppt of hydrofluoric acid, inclusive of 0.70 and 1.3 ppt.

6. The composition according to claim 5 which further includes from about 0.070 ppt to about 0.13 ppt fluorinated alkyl ester surfactant molecules inclusive of 0.070 and 0.13 ppt.

7. A composition for coating or touching up or both coating and touching up a metal surface, said composition being made by mixing together a first mass of water and at least the following components:

(A) a second mass of a water-soluble source of fluorometallate anions to provide in the composition from about 0.5 mM/kg to about 240 mM/kg of the fluorometallate anion, each of said anions consisting of:

(i) at least four fluorine atoms; and

(ii) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron; and, optionally, one or both of

(iii) at least one ionizable hydrogen atom, and

(iv) at least one oxygen atom;

(B) a third mass of one or more water-soluble sources of phosphorus-containing inorganic oxyanions, phosphonate anions or both phosphorus-containing inorganic oxyanions and phosphonate anions; to provide in the composition from about 0.5 g/l to about 10 g/l, calculated as their stoichiontic equivalent of H_3PO_4; and

(C) a fourth mass of a water-soluble source of hexavalent chromium cations to provide the composition with from about 0.5 g/l to about 3.5 g/l of hexavalent chromium cation,

(D) a fifth mass of a component to provide the composition with from about 0.10 g/l to about 2.20 g/l of chromium(III) cation.

8. The composition according to claim 7, wherein:

the fourth mass comprises hexavalent chromium in an amount that corresponds, after any reaction with any reducing agents for hexavalent chromium that are mixed together with it to constitute said composition, to a concentration of residual hexavalent chromium in said composition that is within a range from about 0.50 g/l to about 3.5 g/l.

9. The composition according to claim 8, wherein:

the second mass comprises fluorozirconate anions in an amount that corresponds to a concentration, in said composition, that is within a range from about 3.50 mM/kg to about 6.0 mM/kg, inclusive of 3.50 mM/kg and 6.0 mM/kg;

the third mass corresponds to a total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4, that is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the fourth mass comprises chromic acid in an amount that corresponds to a total concentration, in said composition, of hexavalent chromium ions that is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

is the source of hexavalent chromium for the composition; and

together with a sixth mass of reducing agent that is also mixed into the composition, is also the source of the trivalent chromium ions for the composition, and

said sixth mass of reducing agent corresponds stoichiometrically, in its reaction with chromic acid, to a concentration, in said composition, of chromium(III) ions that is within a range from about 1.25 mM/kg to about 2.20 mM/kg, inclusive of 1.25 mM/kg and 2.20 mM/kg;

wherein a ratio of hexavalent chromium to chromium(III) ions that is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00;

there is also mixed into said composition a seventh mass of fluorinated alkyl ester surfactant molecules that corresponds to a concentration, in said composition, that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

10. The composition according to claim 7, wherein:

the second mass comprises fluorozirconate anions in an amount that corresponds to a concentration, in said composition, of fluorozirconate anions that is within a range from about 18 mM/kg to about 30 mM/kg, inclusive of 18 and 30 mM/kg;

the third mass corresponds to a total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as its stoichiometric equivalent as H_3PO_4, that is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l; the fourth mass comprises chromic acid in an amount that:

corresponds to a total concentration, in said composition, of hexavalent chromium atoms that is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

is the source of hexavalent chromium for the composition; and

together with a sixth mass of reducing agent that is also mixed into the composition, is also the source of the trivalent chromium ions for the composition; and

said sixth mass of reducing agent corresponds stoichiometrically, in its reaction with chromic acid, to a concentration, in said composition, of chromium(III) ions that is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l;

there is a ratio of hexavalent chromium to chromium(III) ions that is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00;

there is additionally mixed into said composition an eighth mass of hydrofluoric acid that corresponds to a concentration, in said composition, that is within a range from about 0.70 to about 1.3 ppt, inclusive of 0.70 and 1.3 ppt; and

there is also mixed into said composition a seventh mass of fluorinated alkyl ester surfactant molecules that corresponds to a concentration, in said composition, that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

11. A process for coating or touching up or both coating and touching up a surface, said surface comprising at least one area of bare metal, at least one area of coating over an underlying metal substrate, or both of at least one area of bare metal and at least one area of coating over an underlying metal substrate, said process comprising operations of:

(I) covering the surface to be coated, touched up, or both coated and touched up with a layer of a liquid composition of claim 1; and

(II) drying the liquid layer formed in operation (I).

12. The process according to claim 11, wherein:

the surface comprises at least one area of bare metal and at least one area of coating over an underlying metal substrate; and

in operation (I), the liquid layer is formed over the at least one area of bare metal.

13. The process according to claim 11, wherein, in said liquid composition used in operation (I):

the fluorometallate anions are selected from the group consisting of fluorosilicate, fluorotitanate, and fluorozirconate anions.

14. The process according to claim 11, wherein, in said liquid composition used in operation (I):

the fluorometallate anions include fluorozirconate anions;

the concentration of fluorozirconate anions is within a range from about 3.5 to about 6.0 mM/kg, inclusive of 3.5 and 6.0 mM/kg,

the total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4, is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the concentration of hexavalent chromium is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

the concentration of chromium(III) ions is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l; and wherein, a ratio of hexavalent chromium to chromium(III) ions is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00; and

the composition further includes a surfactant comprising fluorinated alkyl ester molecules in a concentration that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

15. The process according to claim 14, wherein:

the surface comprises at least one area of bare metal adjacent to at least one area of coating over an underlying metal substrate, said at least one area of coating over an underlying metal substrate comprising a first portion and a second portion, in operation (I), the liquid layer is formed over both the area of bare metal and at least the first portion of said adjacent area of coating over an underlying metal substrate; and

the coating over an underlying metal substrate is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conver-

sion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorosilicate, fluorotitanate, and fluorozirconate.

16. The process according to claim 13, wherein, in the liquid composition used in operation (I):

the fluorometallate anions include fluorozirconate anions;

the concentration of fluorozirconate anions is within a range from about 18.0 to about 30 mM/kg inclusive of 18.0 and 30.0 mM/kg;

the total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4, is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the concentration of hexavalent chromium is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

the concentration of chromium(III) ions is within a range from about 1.25 to about 2.20.g/l, inclusive of 1.25 and 2.20 g/l;

a ratio of hexavalent chromium to chromium(III) ions that is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00;

a concentration of hydrofluoric acid that is within a range from about 0.70 to about 1.3 ppt, inclusive of 0.70 and 1.3 ppt; and wherein

the composition includes fluorinated alkyl ester surfactant molecules in a concentration that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

17. A process for coating or touching up or both coating and touching up a surface, said surface comprising at least one area of bare metal, at least one area of coating over an underlying metal substrate, or both of at least one area of bare metal and at least one area of coating over an underlying metal substrate, said process comprising operations of:

(I) covering the areas to be coated, touched up, or both coated and touched up with a layer of a liquid composition, said liquid composition having been made by mixing together a first mass of water and at least the following components:

(A) a second mass of a water-soluble source of fluorometallate anions to provide in the composition from about 0.5 mM/kg to about 30 mM/kg of the fluorometallate anion, each of said anions consisting of:

(i) at least four fluorine atoms; and

(ii) at least one atom of an element selected from the group consisting of titanium, zirconium, hafnium, silicon, aluminum, and boron; and, optionally, one or both of

(iii) at least one ionizable hydrogen atom; and

(iv) at least one oxygen atom;

(B) a third mass of one or more water-soluble sources of phosphorus-containing inorganic oxyanions, phosphonate anions or both phosphorus-containing inorganic oxyanions and phosphonate anions; to provide in the composition from about 0.5 g/l to about 10 g/l, calculated as their stoichiontic equivalent or H_3PO_4; and

(C) a fourth mass of a water-soluble source of hexavalent chromium cations to provide the composition with from about 0.5 g/l to about 3.5 g/l of hexavalent chromium cation;

(D) a fifth mass of component to provide the composition with from about 0.10 g/l to about 2.20 g/l of chromium(III) cation,

said composition not comprising more than about 0.060% of dispersed silica and silicates; and

(II) drying into place over the surface the liquid layer formed in operation (I).

18. The process according to claim 17, wherein:

the surface comprises at least one area of bare metal and at least one area of coating over an underlying metal substrate; and

in operation (I), the liquid layer is formed over the at least one area of bare metal.

19. The process according to claim 17, wherein the liquid composition further comprises from about 0.70 to about 1.3 ppt of hydrofluoric acid.

20. The process according to claim 19, wherein:

the second mass comprises fluorozirconate anions in an amount that corresponds to a concentration, in said composition, that is within a range from about 3.50 mM/kg to about 6.0 mM/kg, inclusive of 3.50 and 6.0 mM/kg;

the third mass corresponds to a total concentration of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as their stoichiometric equivalent as H_3PO_4, that is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the fourth mass comprises chromic acid in an amount that:

corresponds to a total concentration, in said composition, of hexavalent chromium cations that is within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

is the source of hexavalent chromium for the composition; and

together with a sixth mass of reducing agent that is also mixed into the composition, is also the source of the trivalent chromium ions for the composition; and

said sixth mass of reducing agent corresponds stoichiometrically, in its reaction with chromic acid, to a concentration, in said composition, of chromium(III) ions that is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l;

wherein a ratio of hexavalent chromium to chromium(III) ions is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00;

there is also mixed into said composition a seventh mass of fluorinated alkyl ester surfactant molecules that corresponds to a concentration, in said composition, that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

21. The process according to claim 20, wherein:

the surface comprises at least one area of bare metal adjacent to at least one area of coating over an underlying metal substrate, said at least one area of coating over an underlying metal substrate comprising a first portion and a second portion;

in operation (I), the liquid layer is formed over both the area of bare metal and at least the first portion of said adjacent area of coating over an underlying metal substrate; and

the coating over an underlying metal substrate is selected from the group consisting of a phosphate conversion coating, a chromate conversion coating, and a conversion coating produced by contacting a predominantly aluminiferous or a predominantly zinciferous surface with an acidic treating solution comprising at least one of fluorosilicate, fluorotitanate, and fluorozirconate.

22. The process according to claim 19, wherein:

the second mass comprises fluorozirconate anions in an amount that corresponds to a concentration, in said composition, of fluorozirconate anions that is within a range from about 18 to about 30 mM/kg, inclusive of 18 and 30 mM/kg;

the third mass corresponds to a total condition of phosphorus-containing inorganic oxyanions and phosphonate anions, calculated as its stoichiometric equivalent as H_3PO_4, that is within a range from about 0.50 to about 1.00 g/l, inclusive of 0.50 and 1.00 g/l;

the fourth mass comprises chromic acid in an amount that:

corresponds to a total concentration, in said composition, of hexavalent chromium cations within a range from about 2.25 to about 3.5 g/l, inclusive of 2.25 and 3.5 g/l;

is the source of hexavalent chromium for the composition; and

together with a sixth mass of reducing agent that is also mixed into the composition, is also the source of the trivalent chromium ions for the composition; and

said sixth mass of reducing agent corresponds stoichiometrically, in its reaction with chromic acid, to a concentration, in said composition, of chromium(III) ions that is within a range from about 1.25 to about 2.20 g/l, inclusive of 1.25 and 2.20 g/l;

in said liquid composition, there is a ratio of hexavalent chromium to chromium(III) ions that is within a range from about 2.5:1.00 to about 1.30:1.00, inclusive of 2.5:1.00 and 1.30:1.00;

there is additionally mixed into said composition an eighth mass of hydrofluoric acid that corresponds to a concentration, in said composition, that is within a range from about 0.70 to about 1.3 ppt, inclusive of 0.70 and 1.3 ppt;

there is also mixed into said composition a seventh mass of fluorinated alkyl ester surfactant molecules that corresponds to a concentration, in said composition, that is within a range from about 0.070 to about 0.13 ppt, inclusive of 0.070 and 0.13 ppt.

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